

**ROLE OF CHLORIDE IN
HOT SALT STRESS-CORROSION CRACKING
OF TITANIUM-ALUMINUM ALLOYS**

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ABSTRACT

Experimental evidence obtained by the electron microprobe, mass spectrometer, and radiotracers demonstrated that the role of chloride in hot salt stress-corrosion cracking of titanium-aluminum alloys is to form HCl through a pyrohydrolytic reaction between the salt, moisture retained in the salt deposit, and the protective oxide film on the metal. The HCl subsequently reacts with the metal surface to produce the metal chloride and hydrogen.

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INTRODUCTION

The National Aeronautics and Space Administration has sponsored a research program at Savannah River Laboratory to develop fundamental knowledge about the mechanism of hot salt cracking of titanium-aluminum alloys. These alloys are important in the design of supersonic aircraft which will operate with skin temperatures as high as 290°C (550°F) while contaminated with sea salt. The main emphasis was placed on the Ti-8Al-1Mo-1V alloy in this work. In laboratory tests, this and similar alloys are susceptible to hot salt cracking under the conditions that could occur during operation of supersonic transports.

The objective of the work described in this report was to define the role of chloride in the hot salt stress-corrosion phenomenon. Previous workers¹ have proposed that the salt-metal reactions produce chlorine gas which causes cracking by localized, stress-accelerated attack. In contrast, studies at SRL² indicated that HCl gas, rather than chlorine, is produced during salt-metal reactions, and that exposure to HCl gas alone can cause cracking of stressed specimens without salt deposits. The SRL studies also showed that some form of chloride was strongly adsorbed on titanium alloy specimens that were wetted by aqueous salt solutions at room temperature and subsequently rinsed and dried such that no salt deposits were left on the surface. These observations raised the question of whether the chloride was initially adsorbed as equivalent amounts of H^+ and Cl^- or as complex chloride ions in the metal oxide film.

In the present work, the chloride-adsorption phenomenon was studied as a function of pH of the initial salt solution, and the salt-metal reactions were investigated further.

Radiotracer techniques, electron microprobe analysis of cracked specimens, and mass spectrometric analysis of volatile corrosion products were employed in these studies. The experiments were successful in identifying the compound that initiates the crack, and have indicated several possible mechanisms for the remainder of the hot salt stress-cracking process.

SUMMARY

The role of chloride in hot salt cracking of Ti-Al alloys is to form hydrogen chloride by a pyrohydrolytic reaction involving the chloride salt, water and probably aluminum oxide. The hydrogen chloride penetrates the protective oxide film and attacks the underlying metal, thereby forming a metal chloride and hydrogen.

- a) Chloride ion and water are rapidly adsorbed on the surface of titanium alloys during contact between the alloy surface and a salt solution.
- b) Hydrogen chloride is produced at elevated temperatures by pyrohydrolysis of sodium chloride.
- c) Only HCl, H₂O and H₂ are observed as volatile products of heating a mixture of titanium alloy chips and salt.
- d) The chloride ion concentration generally decreases toward the tip of the crack produced during hot salt exposures; sodium ion remains at the surface.
- e) The pH of the salt solution used to deposit the salt on the metal surface strongly affects the rate of crack nucleation. Cracks nucleate sooner at higher hydrogen ion concentrations.

Although most of the work has been done with sodium chloride, bromide and iodide salts also cause hot salt cracking by similar mechanisms, and the relative severity of the cracking may simply be due to the ability of the halide to penetrate the oxide and react with the underlying metal. Fluoride salts did not cause cracking in these tests.

DISCUSSION

EXPERIMENTAL PROCEDURES

Preparation of Specimens

The test specimens were metallographically polished $\frac{3}{4}$ - x $\frac{3}{8}$ - x 0.050-in. strips of duplex-annealed³ Ti-8Al-1Mo-1V alloy. The strips were mounted in 4-point loading holders and stressed by bending to a surface-fiber stress of 10^5 psi unless otherwise specified. A standard beam deflection formula was used to calculate stress.⁴

A few drops of a salt solution were placed on the stressed sample and then dried at 110°C for 1 hour. The samples were normally heated to 343°C (650°F) in a furnace with an air atmosphere.

Salt solutions were prepared from reagent-grade chemicals and their pH was adjusted with sodium hydroxide or with a halogen acid corresponding to the anion of salt. Solutions of $^{22}\text{NaCl}$ or Na^{36}Cl were prepared similarly.

Specimens for adsorption studies were immersed in radioactive solutions. The activity of these solutions was monitored and tracer was added if the activity decreased by 5%; pH was also held constant.

Electron Microprobe Analysis

A Materials Analysis Model 400 electron microprobe was used to determine Na and Cl in cracks and adjacent regions. X-rays were diffracted with a potassium acid phthalate crystal for Na and a pentaerythritol crystal for Cl. Spectrometers were calibrated with carbon-coated sodium chloride crystals.

Mass Spectrometer Analysis

A Consolidated Engineering Corp. Model 21-103 mass spectrometer was used to analyze volatile corrosion products that were evolved when mixtures of Ti-8Al-1Mo-1V alloy and sodium chloride were heated in a closed glass reaction vessel attached directly to the mass spectrometer. The salt solution was dried on the titanium alloy chips for 1 hour at 110°C . Chips were used to assure a high surface area/salt ratio. The pressure in the reaction vessel containing the salt-coated chips was reduced so that at temperature, without a reaction, the pressure would be 1 atmosphere. Temperature was monitored in a thermocouple well inserted into the chips. About 2% of the gas in the reaction vessel was removed each time a sample was taken. The stopcocks in the reaction vessel and on the mass spectrometer were greased

with "Kel-F"*, a lubricant unattacked by Cl_2 and other strong oxidants.

Further details on specimen preparation unique to a particular experimental approach are discussed under Results.

RESULTS

Ion Adsorption on Metallic Surfaces

Sodium and chloride ion adsorption on the surfaces of a variety of metals was studied by radiotracer techniques to determine if, as previously established for several titanium-aluminum alloys,¹ the chloride ion (Cl^-) was preferentially adsorbed. Test samples were exposed for 15 minutes at room temperature to solutions of $^{22}\text{NaCl}$ or Na^{36}Cl in water, pH 5-6. The exposed samples were rinsed in flowing hot water for one minute and then were analyzed for ^{22}Na or ^{36}Cl by radiocounting techniques. The results, Table I, showed that Cl^- was selectively adsorbed on all of the metals tested.

TABLE I

Adsorption of Na^+ and Cl^- on Selected Metals

<u>Material</u>	<u>Surface Condition</u>	<u>Adsorption, $\mu\text{g}/10 \text{ cm}^2$</u>	
		<u>Na^+</u>	<u>Cl^-</u>
Type 304 Stainless Steel	Polished	0.00	12.0
Titanium	Polished	0.00	12.0
Ti-8Al-1Mo-1V	Polished	0.14	10.0
Ti-8Al-1Mo-1V	Mill Oxide	0.03	9.4
Tantalum	Oxidized	0.01	10.0
Zircaloy-2	Oxidized	0.03	8.5
Platinum	Oxidized	0.00	4.5

* Trademark of Minnesota Mining and Manufacturing Company, St. Paul, Minnesota.

To maintain electrical neutrality, the charge associated with the chloride adsorption must be balanced by adsorption of an equal positive charge (H^+ since Na^+ was not adsorbed), oxidation of a cation in the oxide (e.g., Ti^{++} to Ti^{+++}), or some balancing change in the defect structure of the oxide film.

Previous studies² had established that hydrogen (3H) was adsorbed during titanium alloy exposures to salt-water solutions, but it was not clear if the hydrogen was adsorbed as $^3H^+$ associated with Cl^- or as 3H_2O . If the hydrogen ion was acting to neutralize the negative Cl^- charge, then chloride adsorption should be directly proportional to hydrogen ion concentration and should be a maximum when the hydrogen ion concentration is high (i.e., pH is low).

Experiments summarized in Figure 1 showed that chloride adsorption on metallographically polished Ti-8Al-1Mo-1V samples immersed in $Na^{36}Cl-H_2O$ solutions immediately after polishing was a maximum in nearly neutral solutions and decreased as the pH of the solution increased or decreased. Samples that were exposed to air at 20°C and 50% relative humidity overnight and then immersed in the chloride tracer solution showed a similar pH maximum and an overall increase in chloride adsorption. This increase in adsorption was probably due to the increase in oxide film thickness. Thus, hydrogen ion adsorption is not the mechanism for maintaining charge neutrality, and hydrogen was adsorbed as H_2O in the previous studies at room temperature.²

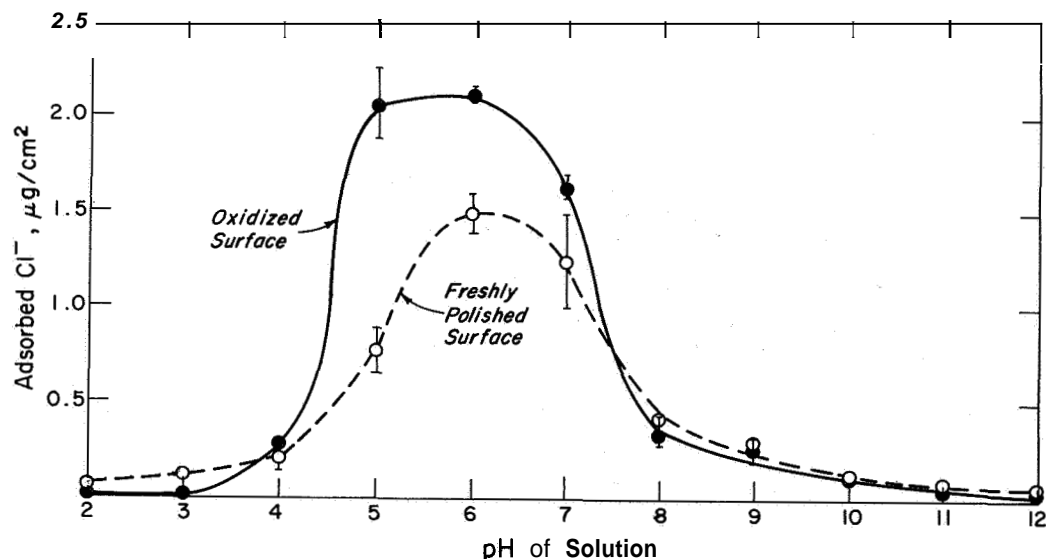


FIG. 1 CHLORIDE ADSORPTION ON SURFACE OF Ti-8Al-1Mo-1V ALLOY

The reason for the increase in chloride adsorption in approximately neutral solutions was not clearly established. However, similar trends in chloride adsorption were noted for other heavily oxidized Ti-Al alloy samples that retained a visible, intact oxide throughout the tests. Therefore, one possible mechanism can be eliminated; namely, that the pH effects cannot be attributed to dissolution of the oxide films in the basic or acidic solutions and to a corresponding decrease in adsorption on the clean metal surfaces.

Volatile Corrosion Products

Reactions involving HCl, Cl₂, H₂O, TiCl₂ and other volatile species have been proposed as steps in the hot salt cracking sequence.^{1,2)} If these species are involved in the cracking process, they should also be produced when mixtures of titanium chips and NaCl are heated to elevated temperatures. To test for the presence of these species, mixtures of titanium chips and NaCl were heated to 260 and 400°C (500 and 750°F) in closed reaction vessels. Gas samples taken from the vessel after various exposure times were analyzed by mass spectroscopy. Spectral data were collected to mass 170 in the event that TiCl₂ or TiCl₃ might be observed. However, these compounds were not expected since titanium chlorides readily hydrolyze at the exposure temperature and produce hydrogen and HCl.

Only H₂O, HCl and H₂ were detected as volatile products as shown in Table 11. Water was associated with the NaCl either by adsorption or as inclusions. The concentration of HCl was relatively constant, and increased only slightly with time; the H₂ concentration increased markedly, particularly during the early stage of exposure, Figure 2.

TABLE II

Volatile Products from
NaCl-Coated Ti-8Al-1Mo-1V Chips

Mass No.	Volatile Product	Contributors to Product	
		Mass No.	Presence of Product
2	H ₂	H ₂ O, HCl	Yes
18	H ₂ O	-	Yes
35	Cl	HCl	No
36	HCl	-	Yes
37	Cl	HCl	No
70	Cl ₂		NO
74	Cl ₂	-	No

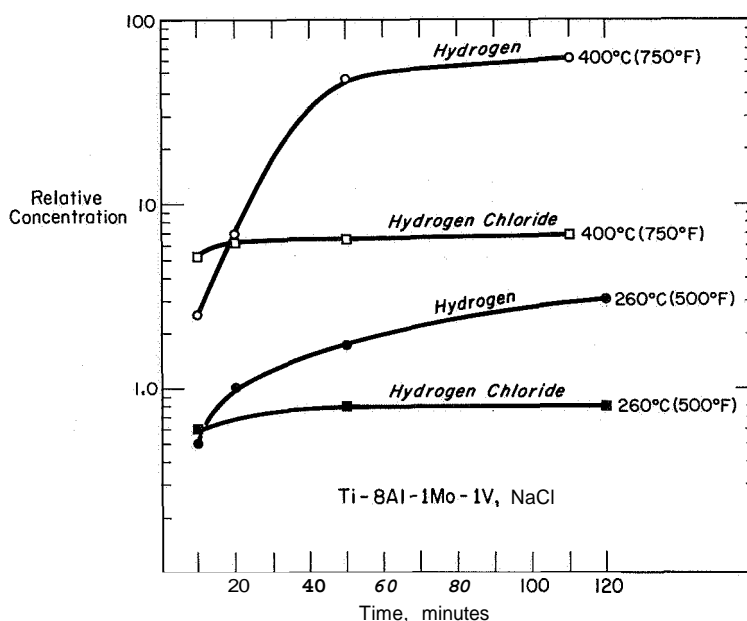


FIG. 2 EVOLUTION OF H_2 AND HCl DURING HOT SALT CORROSION

Ion Penetration into Cracks

The penetration of sodium and chloride ions into cracks was measured by electron microprobe techniques to explain the role of the corrosion products in hot-salt cracking. Samples that were cracked during exposures to NaCl at $343^\circ C$ ($650^\circ F$) were polished in nonaqueous lubricants so that the crack cross section could be scanned by an expanded, 8μ , electron beam. Care was taken to prevent sodium chloride from being forced into the crack during sample preparation. Seven cracks were examined. Cracks were 75μ to 320μ deep.

The microprobe analysis showed that, in general, sodium was concentrated at the mouth of the crack and that chloride concentration decreased from the mouth toward the crack tip. A typical crack and the accompanying sodium and chloride concentration profiles are shown in Figure 3. These results showed that chloride was penetrating the crack in some form other than NaCl. Mass spectrographic analyses showed HCl, not Cl_2 .

The penetration of chloride but not sodium was supported by autoradiographic studies of samples cracked with $^{22}NaCl$ and $Na^{36}Cl$. Samples that had cracked during 2 weeks exposure at $343^\circ C$ were rinsed in H_2O , mechanically polished to remove 50μ from the metal surface, then autoradiographed. The chloride ion, but not sodium, was found concentrated in the cracked regions, as shown in Figure 4.

Cross Section of Crack

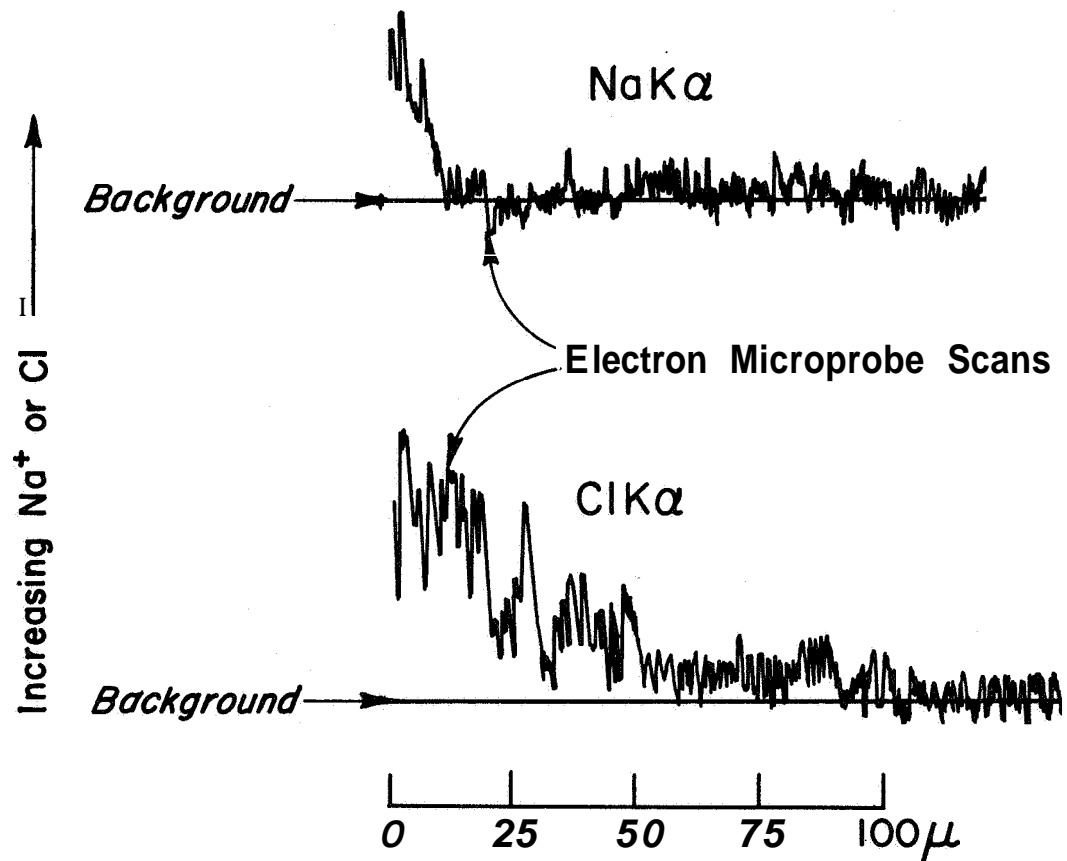
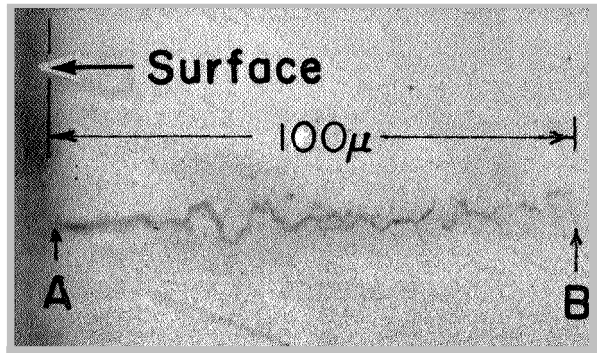
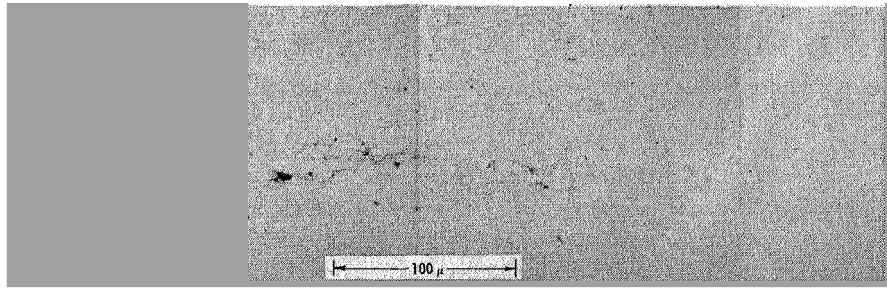
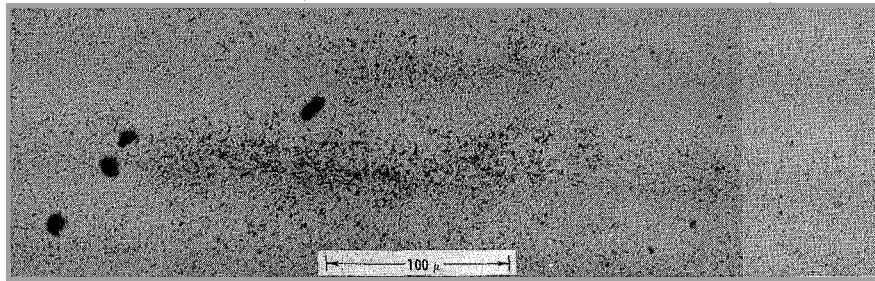


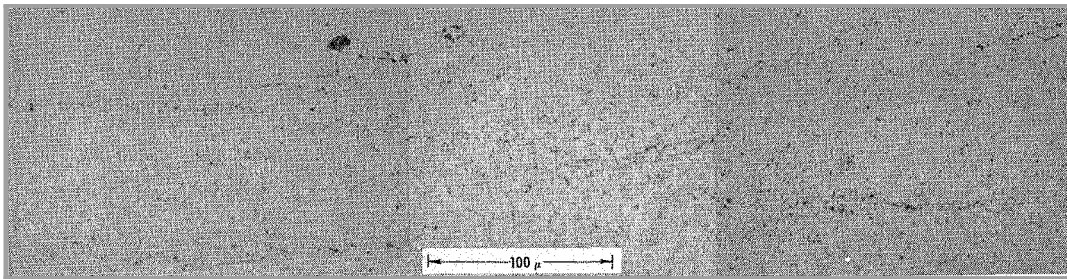
FIG. 3 VARIATION OF SODIUM AND CHLORIDE CONCENTRATION WITHIN CRACK
(Hot Salt Stress Cracked Ti-8Al-1Mo-1V)



a. Subsurface Crack - Photomicrograph of crack after removal of $\sim 50\mu$ of surface metal. Original stressed surface exposed to Na^{36}Cl for 2 weeks at 343°C



b. ^{36}Cl Autoradiograph - Reveals concentration of chlorides $\sim 50\mu$ below original surface in areas of cracks. Smearing of activity in vicinity of cracks is probably due to dispersion of chloride removed from cracks in polishing.

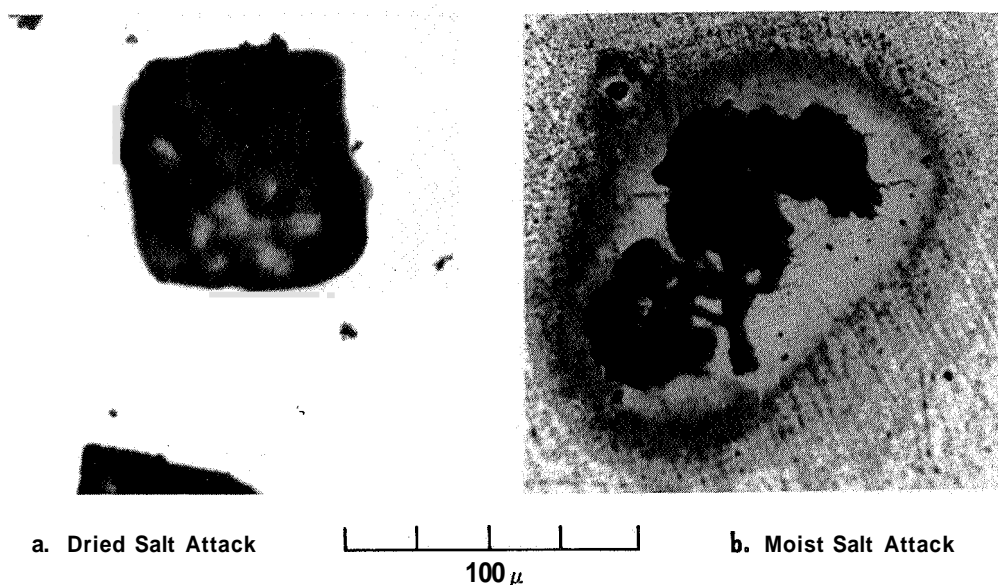


c. ^{22}Na Autoradiograph - Original surface exposed to $^{22}\text{NaCl}$ for 2 weeks at 343°C . No concentration of Na evident 50μ below original surface in areas of cracks. Tracks are background.

FIG. 4 AUTORADIOGRAPHS OF STRESS-CORROSION CRACKS
[Ti -8Al-1Mo-1V Alloy cracked by radioactive NaCl at 343°C (650°F)]

Effect of Moisture

Moisture is required for the hot salt stress-corrosion cracking process. Hot salt stress-corrosion cracking of titanium alloys at 343°C was not initiated when the reagents and metal were dried. In the presence of moisture, cracking was initiated with NaCl after 80 minutes at 343°C . Figure 5 shows the effect of moisture in two identical specimens after 90 minutes (10 minutes after initiation). The dry system, in which the salt was dried 3 days at 343°C , did not crack the metal even when the test was extended to 10,800 minutes (7 days). The moist system showed attack and cracking in 90 minutes.



Both specimens polished, stressed, treated with salt, and heated at 343°C (650°F) for 90 minutes. Note absence of attack when salt and specimens are maintained in the anhydrous state as opposed to the stains and cracks produced in the moist specimen.

FIG. 5 EFFECT OF MOISTURE ON HOT SALT STRESS-CORROSION CRACKING

Cracking in Other Halide Salts

Hot salt cracking of titanium alloys has generally been ascribed to some chloride salt, although it has been established that other sodium halide salts will produce less severe cracking. Further studies of the effect of halide ion on cracking time were made to determine the role of the anion in crack initiation.

Table III shows the time required for crack initiation in samples exposed to various halide salts deposited from saturated salt solutions. The rate of crack initiation appeared to be a function of the size of the halide ion; the effectiveness of the ion in promoting cracking increased (i.e., $\text{Cl} > \text{Br} > \text{I}$) as the size of the ion decreased. The fluoride did not cause cracking in any samples but did cause generalized pitting.

The pH of the saturated salt solution that was applied to the specimen was also found to be important; crack initiation increased with decreasing pH (Table III). This demonstrates the importance of the hydrogen ion in the cracking process; cracking was most rapid when the hydrogen ion concentration was high.

TABLE III

Effect of pH on Time to Cracking
Caused by Various Dried Salts

Salt	pH of Saturated Solution	Temp, °C	Time to Cracking, min	pH of Adjusted Solution	Time to Cracking, min
NaCl	4.1	343(650°F)	80	0.5	40
NaBr	4.7	343(650°F)	150	0.5	75
NaI	8.9	400(750°F)	150	0.5	75
NaF	8.4	400(750°F)	>15,000*	5.2	>240*
$\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$	0.2	343(650°F)	10	4.1	30
$\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$	0.2	343(650°F)	10	0.5	15
CuCl	3.4	343(650°F)	60	0.5	15

* Specimen did not crack; pH could not be made highly acidic because of HF association.

ROLE OF CHLORIDE

The reaction of water with a hydrolyzable salt at elevated temperature is termed pyrohydrolysis. This reaction is often used for the analysis of halide salts because a volatile species of the halogen is formed (e.g., HCl, HBr).⁵ Aluminum oxide or vanadium pentoxide are often added as accelerators when the salt is difficult to hydrolyze, as is NaCl.

The experimental evidence demonstrates that pyrohydrolysis occurs in the cracking process. The requisites for pyrohydrolysis are present: 1) heat, 2) water, adsorbed or present as inclusions in the NaCl, 3) accelerators for difficulty hydrolyzable salts are present in the form of aluminum or vanadium oxides in the protective film on Ti-8Al-1Mo-1V alloy. In addition, HCl has been shown to be a corrosion product and moisture was shown to be necessary for cracking.

The remainder of the cracking sequence that follows the acid attack is now being investigated in a companion study. The process may involve a) participation of H^+ as an embrittling agent (Hydrogen Embrittlement), b) the action of Cl^- or H^+ as a bond weakener (Stress-Sorption Cracking), or c) localized corrosion by HCl attack (Electrochemical Mechanism).

REFERENCES

1. V. C. Petersen and H. B. Bomberger. "The Mechanism of Salt Attack on Titanium Alloy." Stress Corrosion Cracking of Titanium, STP 397, American Society for Testing Materials, Philadelphia, Pa., p. 80 (1966).
2. S. P. Rideout, M. R. Louthan, Jr., and C. L. Selby. "Basic Mechanism of Stress Corrosion Cracking of Titanium." Stress Corrosion Cracking of Titanium, STP 397, American Society for Testing Materials, Philadelphia, Pa., p. 137 (1966).
3. R. A. Wood. A Tabulation of Designations, Properties and Treatments of Titanium and Titanium Alloys. DMIC Memorandum 171, Battelle Memorial Institute, Columbus, Ohio (1963).
4. L. L. Shreier, "Corrosion", Vol. 11, p. 20.59, John Wiley and Sons, New York, N. Y. (1963).
5. C. J. Rodden, "Analytical Chemistry of the Manhattan Project", p. 729, McGraw-Hill Book Co., New York, N. Y. (1950).